J. Org. Chem. **1983**, *48*, 4557–4563 **4557**

Table V. Heats of Solution[a] of Betaine Ethyl Ester Chloride

solvent[b]	ΔH_S, kcal/mol
H_2O	1.56 ± 0.15
0.60 ethanol (aq)	4.03 ± 0.04
0.60 Me_2SO (aq)	4.26 ± 0.04

[a] Integral heats of solution were measured at concentrations of 0.001–0.004 M; the error is given as the standard deviation of the mean of three measurements; temperature 25.0 °C. [b] Composition of mixed solvents is indicated as the mole fraction of the organic component.

In each solvent, initial rates were measured at initial concentrations which had ionic strengths ranging from 0.9×10^{-5} to 1.5×10^{-3}. To obtain a rate constant for the pure solvent, that is, at zero ionic strength, we extrapolated the rate constants obtained from the above initial rates to zero ionic strength by plotting ln k_2 vs. $I^{1/2}$. This gave a linear plot, the intercept being the k_2 at zero ionic strength, and the standard deviation of this intercept being taken as the error of this k_2 value (both tabulated in Table I).

Product Verification. Reaction solutions of betaine ethyl ester chloride and NaOH (10^{-2} M) in H_2O and in 60 mol % aqueous dimethyl sulfoxide as the solvent were subjected to VPC analysis (6-ft Porapak Q column, 150 °C, followed by 220 °C to elute the Me_2SO). In each case, the volatile product was found to be ethanol. No methanol was detected.

Heats of Solution. The integral molar heat of solution of betaine ethyl ester chloride was measured in the three solvents of interest with a LKB-8700 calorimeter (see Table V).

Acknowledgment. This work was supported in part by a grant from the City University of New York Faculty Research Award Program.

Registry No. Betaine ethyl ester chloride, 3032-11-9.

Photosensitized (Electron-Transfer) Rearrangements of Cinnamyl Alcohol Derivatives

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Specific electron-donor compounds are capable of photosensitizing the rearrangement and solvolysis of several cinnamyl alcohol derivatives. Under suitable conditions, the formation of rearranged α-phenylallyl derivatives occurs in synthetically useful yields. The intermediates in this process have ionic character and have been trapped by methanol as methyl ether derivatives. The ability of the photosensitizers to effect these electron-transfer-initiated reactions correlates well with the enthalpy of reaction calculated by the Weller equation.

Introduction

The reactions of organic molecules with photoexcited sensitizers leading to electron-transfer processes or to exciplex formation have received considerable attention in recent years. In many of these instances, electronic energy transfer is endothermic and the processes leading to new product formation are dependent upon the electron-donating and -accepting properties of the quencher and the excited state. Solvent polarity, excitation energies, and redox potentials of the reaction partners play a critical role in determining if such processes may occur.[1-4] The free energy (ΔG) associated with these processes can be calculated by using the expression developed by Weller[5] (eq 1). In this expression E_D^{oxidn} and E_A^{redn} are the electrochemically determined potentials for the one-electron oxidation of the donor and reduction of the acceptor, respectively. $\Delta E(S^*)$ is the 0–0 transition energy of the excited state of the light-absorbing sensitizer for this process.

$$\Delta G = (E_D^{\text{oxidn}} - E_A^{\text{redn}}) - \Delta E(S^*) \qquad (1)$$

A number of reports have appeared recently in which photoexcited donor molecules affect ionic-like reactions with suitable acceptor substrates. Arnold[6] has shown that electron-donating photosensitizers will catalyze the addition of alcohols and of HCN to olefins when the requirements of the Weller equation (eq 1) are met. Similarly, Yonemitsu[7] reported the photochemical removal of an *N*-tosyl protecting group from *p*-toluenesulfonamides by using electron-donating sensitizer compounds. In 1976, Ullman and co-workers described the photosolvolysis of certain benzyl alcohol derivatives.[8] These reactions appeared to require an intramolecular electron donor (dimethylamino or *p*-(dimethylamino)phenyl) and an acceptor (phenyl) interaction and did not involve classical sensitization by energy transfer. After photoexcitation, an

$$\text{A–CH(OR)–D} \xrightarrow{h\nu} [\cdot^{-}\text{A–CH(OR)–D}^{+}\cdot] \rightarrow \text{A–}\dot{\text{C}}\text{H–D}^{+}\cdot + {}^{-}\text{OR} \rightarrow \text{A–}{}^{+}\text{CH–D} + {}^{-}\text{OR}$$

intermediate phenyl radical anion ($A^{-}\cdot$) is generated that expels acetate or hydroxide ion to give a benzyl radical. This new intermediate is then reoxidized by the electron-deficient donor (radical cation, $D^{+}\cdot$) to generate a ground-state carbenium ion that produces the observed products. Cristol et al.[9] have reported several examples of photochemically induced Wagner–Meerwein rearrangements and attendant photosolvolyses in allylic substrates capable of intramolecular electron transfer.

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[1] Weller, A. "The Exciplex"; Gordon, M. S., Ware, W. R., Eds.; Academic Press: New York, 1975; Chapter 2.

[2] Arnold, D. R.; Morchat, R. M. *Can. J. Chem.* **1977**, *55*, 393. Wong, P. J.; Arnold, D. R. *Ibid.* **1979**, *57*, 1037.

[3] Brown-Wensley, K. A.; Mattes, S. L.; Farid, S. *J. Am. Chem. Soc.* **1978**, *100*, 4162. Mattes, S. L.; Farid, S. *Acc. Chem. Res.* **1982**, *15*, 80.

[4] Padwa, A.; Chow, C. S.; Rieker, W. F. *J. Org. Chem.* **1980**, *45*, 4555.

[5] Weller, A. *Nobel Symp.* **1967**, *5*, 413. Rehm, D.; Weller, A. *Isr. J. Chem.* **1970**, *8*, 259.

[6] Arnold, D. R.; Maroulis, A. J. *J. Am. Chem. Soc.* **1977**, *99*, 7355.

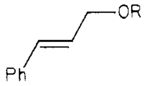
[7] Hamada, T.; Nishida, A.; Matsumoto, Y.; Yonemitsu, O. *J. Am. Chem. Soc.* **1980**, *102*, 3978.

[8] Lin, C-I.; Singh, P.; Ullman, E. G. *J. Am. Chem. Soc.* **1976**, *98*, 6711.

[9] Cristol, S. J.; Graf, G. A. *J. Org. Chem.* **1982**, *47*, 5286. Cristol, S. J.; Strom, R. M. *J. Am. Chem. Soc.* **1980**, *102*, 5577.

0022-3263/83/1948-4557$01.50/0

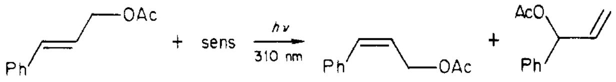
In connection with our interest in the electron-donor properties of various electron-rich aromatic photosensitizers, we undertook a study of the chemistry of organic substrates having potential ionic leaving groups. Since the photochemistry of various cinnamyl derivatives had previously been examined,[10-14] this system appeared to offer a sensible basis set within which to further evaluate "endothermic photosensitization" processes. We report here our studies on the photosensitized rearrangements and solvolyses of cinnamyl alcohol derivatives 1–4 which we believe can best be rationalized in terms of electron-transfer processes.



1, R = C(O)CH_3
2, R = C(O)Ph
3, R = H
4, R = CH_3

Results

We initially examined the acetone-sensitized excited triplet state behavior of *trans*-cinnamyl acetate in acetonitrile. Irradiation of *trans*-cinnamyl acetate (1-*t*) in acetonitrile/acetone (8:2 v/v) for 21 h produced only trans–cis photoisomerization (35% trans, 65% cis; identical with the previous literature report).[14] Contrary to a previous report,[10] no allylic isomerization was noted (<0.5%). Even when cinchonine was used as the sensitizer for an acetonitrile solution of 1-*t*, only very slow formation of the α-phenylallyl acetate (5) was noted after 20.5 h of irradiation (mixture consisted of 37.5% 1-*t*, 60% 1-*c*, and 2.5% 5). Because of the low solubility of cinchonine in acetonitrile, it is possible that 1-*t* and 1-*c* were absorbing a significant portion of the incident light and thus were directly being converted to 5. A control experiment was run in which 1-*t* in acetonitrile was irradiated directly without sensitizer for 2 h. At the end of this time, the reaction mixture contained 93% 1-*t*, 6.3% 1-*c*, and 0.7% 5. Thus, it seems that neither the excited singlet or triplet state of cinnamyl acetate is capable of effecting a significant amount of allylic rearrangement.



1-*t* 1-*c* 5

In contrast to these classical photochemical pathways, we have found that irradiation of cinnamyl acetate in the presence of several electron-donor sensitizers (present in concentrations sufficient to absorb >99% of the incident light) causes facile conversion to the allylic isomer 5. For example, irradiation of a deaerated acetonitrile solution of 1-*t* containing 1,4-dimethoxybenzene (DMB) for 1 h produces a mixture containing 84.9% 1-*t*, 9.3% 1-*c*, and 5.7% 5. After 2-h irradiation, the same mixture contains 73.2% 1-*t*, 16.1% 1-*c*, and 10.7% 5. Similarly, irradiation of an acetonitrile solution of 1-*c* for 70 min with DMB as sensitizer gave a reaction mixture containing 73% 1-*c*, 17% 1-*t*, and 10% 5. A control experiment in which the allylic isomer 5 was irradiated in acetonitrile with DMB revealed that only a small amount of isomerization back to 1-*t* and 1-*c* occurred (after 70 min, 1.6% 1-*t*, 2.4% 1-*c*, and 96.0% 5). Thus, it should be possible to build up significant amounts of the rearranged allylic isomer 5 by continued irradiation of DMB-sensitized solutions of 1. We have found that irradiation of DMB–acetonitrile solutions of 1 for ca. 16 h provides a composition containing 56.5% 5, 27% 1-*c*, and 16.5% 1-*t*. The lack of significant side reactions in these sensitized irradiations gives this isomerization process some synthetic utility. As will be discussed later, use of an acetonitrile/acetic acid solvent system enables this process to become synthetically useful for preparing α-phenylallyl derivatives.

Table I. Effectiveness of Various Sensitizers for Isomerization of *trans*-Cinnamyl Acetate (1-*t*)

sensitizer	irrad time, h	1-*t*, %	1-*c*, %	5, %
acetone	2	67.5	32.5	
1,4-dimethoxybenzene	2	73.2	16.1	10.7
9,10-dimethoxy-2-ethylanthracene	22.8	62.6	35.7	1.7
2-methoxynaphthalene	21.3	58.7	41.3	
N,N-dimethylaniline	1.3	86.1	9.4	4.5
naphthalene	2.3	33.2	66.8	
p-xylene	3.25	79.1	11.7	9.2

To elucidate the nature of the energy-transfer process from electronically excited DMB to ground-state 1, we performed a Stern–Volmer quenching experiment using increasing increments of 1,3-pentadiene as the electronic energy acceptor. While the formation of α-phenylallyl acetate (5) was not quenched significantly by piperylene (up to 0.6 M), the formation of the *cis*-cinnamyl acetate was noticeably quenched. Our data further seem to indicate that for the formation of 1-*c* there are two regions of quenching efficiency,[15] and hence two distinct types of excited-state intermediates may be involved. It appears that at least part of the trans–cis isomerization is derived from the excited-state triplet of 1. The lack of piperylene quenching of the formation of 5 could be interpreted as evidence for the involvement of either a singlet excited state of DMB or of a nonquenchable triplet state of DMB. However, this latter possibility seems unlikely in view of the failure of acetone-sensitized experiments to produce significant amounts of 5.

A variety of other potential electron-donor compounds were evaluated as sensitizers for 1. A summary of these experiments is given in Table I.

Clearly, not all sensitizers have the capability of sensitizing the conversion of 1-*t* to 5, although all were reasonably efficient at sensitizing the trans–cis interconversion. Sensitization with naphthalene is particularly interesting, since extended irradiation (5 h) gave a reaction mixture with a far higher cis–trans ratio (81.8:18.2) than that previously reported (cis–trans ratio 65:35). A possible explanation for this observation will be presented in the Discussion section.

The effect of solvent on the photochemistry of 1 with DMB was studied briefly. Use of cyclohexane (dielectric constant, ϵ 2.07)[16] in lieu of acetonitrile (ϵ 37.5)[16] gave a reaction mixture after 2-h irradiation that contained less 1-*c* as well as less rearranged allylic isomer 5 (cf. Table II). These preliminary data seem to suggest that a less polar solvent leads to less sensitized rearrangement. When

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(10) Cookson, R. C.; Gogte, V. N.; Hudec, J.; Mirza, N. A. *Tetrahedron Lett.* **1965**, 3955.

(11) Cristol, S. J.; Lee, G. A.; Noreen, A. L. *J. Am. Chem. Soc.* **1973**, *95*, 7067.

(12) Cristol, S. J.; Micheli, R. P. *J. Org. Chem.* **1975**, *40*, 667.

(13) Cristol, S. J.; Strom, R. M. *J. Am. Chem. Soc.* **1979**, *101*, 5707.

(14) Kadoma, Y.; Ueno, A.; Takeda, K.; Uno, K.; Iwakura, Y. *J. Polym. Sci., Polym. Chem. Ed.* **1975**, *13*, 1545.

(15) For a complete discussion of Stern–Volmer quenching studies on sensitized reactions, see: Cristol, S. J.; Micheli, R. P. *J. Am. Chem. Soc.* **1978**, *100*, 850.

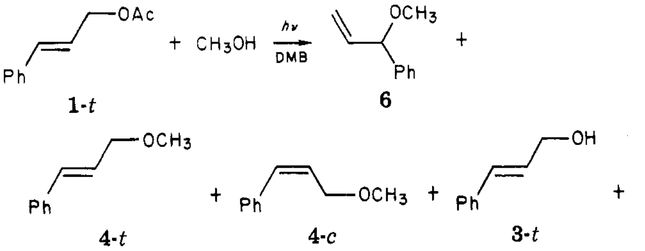
(16) Hine, J. "Physical Organic Chemistry"; McGraw-Hill: New York, 1962; p 39.

Table II. Irradiation of *trans*-Cinnamyl Acetate with 1,4-Dimethoxybenzene in Various Solvents[a]

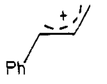
solvent	irrad time, min	1-*t*, %	1-*c*, %	5, %	others, %
CH_3CN	120	73.2	16.1	10.7	
C_6H_{12}	130	88.2	8.8	3.0	*b*
CH_3OH[c]	106	46.6	8.9	7.8	36.8[d]

[a] All solutions ca. 5.5 × 10^{-2} M 1-*t* and ca. 0.1 M DMB. [b] Ca. 10% by GC peak area of three other products that are more volatile than the three allylic acetate products were detectable at this time. [c] Solvent consisted of 3 mL of CH_3OH and 7 mL of CH_3CN; ca. 50 mg of K_2CO_3 added as acid scavenger. [d] Other products detected in this reaction mixture included: 5.5% α-phenylallyl methyl ether; 3.3% *cis*-cinnamyl methyl ether, 25.0% *trans*-cinnamyl alcohol, 3.07% *trans*-cinnamyl methyl ether.

methanol was included in the solvent system, the rate of photochemical rearrangement was not noticeably affected, but interestingly, products of photosolvolysis were formed. A major component of this reaction mixture was *trans*-cinnamyl alcohol (3-*t*), but a control experiment indicated this was merely a product formed in the dark by transesterification of 1-*t* and methanol. No other rearranged products were produced in this dark, control experiment. In the photosensitized isomerization with methanol present, the combined yields of rearranged products (5 + 6) exceeded slightly the amount of 5 formed in pure acetonitrile. Correspondingly, the combined amounts of 1-*t*, 4-*t*, and 3 were approximately the same as the amount of 1-*t* detected when the solvent was pure acetonitrile. Thus, it appears that methanol facilitates the allylic isomerization and is competitive with acetate in trapping the reactive intermediate. That this intermediate is most likely the allylic cation (A) was demonstrated by another control experiment in which cinnamyl alcohol in methanol containing a catalytic amount of *p*-toluenesulfonic acid rearranged in the dark at room temperature. The mixture was analyzed by GC and GC/MS (comparison with authentic samples) to contain 9.6% 6, 67.8% 4-*t*; and 22.6% 3. No cis products were detected.

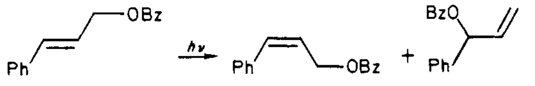


1-*t* 6 4-*t* 4-*c* 3-*t* 1-*c* + 5



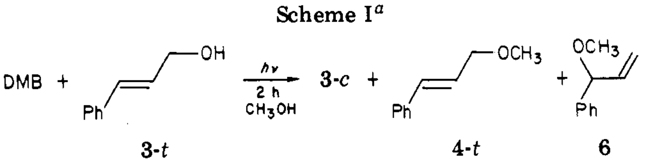
A

Because Cookson[10] had reported that cinnamyl benzoate was photoisomerized more readily than the acetate, we examined this compound under standard conditions. Direct irradiation of 2-*t* in pure acetonitrile for 2 h gave only trans–cis isomerization (83.5% 2-*t*, 16.5% 2-*c*). Under triplet-sensitized conditions (solvent 20:80 acetone–acetonitrile), a mixture containing 50.1% 2-*c*, 48.7% 2-*t*, and 1.2% α-phenylallyl benzoate (7) was obtained after 2 h.



2-*t* 2-*c* 7

Scheme I[a]

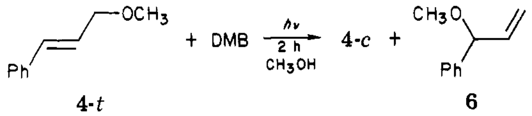


3-*t* 4-*t* 6

experiment	3-*t*		3-*c*	4-*t*	6
A	85.0%		7.9%	3.6%	3.4%
B	79.7%	0.054 g of $KHCO_3$	9.9%	6.7%	3.6%

[a] Conditions: A, [3-*t*] = 6.81 × 10^{-2} M, [DMB] = 0.109 M; B, [3-*t*] = 6.64 × 10^{-2} M, [DMB] = 0.119 M.

Scheme II[a]



4-*t* 6

experiment	4-*t*		4-*c*	6
A	80.7%		13.5%	5.8%
B	81.3%	0.054 g of $KHCO_3$	11.8%	6.9%

[a] Conditions: A, [4-*t*] = 6.2 × 10^{-2} M, [DMB] = 0.12 M; B, [4-*t*] = 6.6 × 10^{-2} M, [DMB] = 0.11 M.

When DMB was employed as the sensitizer, a significant amount of allylic isomerization occurred. After 1-h irradiation, a DMB–acetonitrile solution of 2-*t* gave 82.4% 2-*t*, 12.0% 2-*c*, and 2.6% 7; after 2-h irradiation, a similar solution was analyzed to contain 77.5% 2-*t*, 18.5% 2-*c*, and 4.2% 7. Thus, under our conditions, it does not appear that cinnamyl benzoate is more readily photoisomerized than its acetate analogue.

Although allylic and benzylic alcohols are generally stable to photosolvolysis conditions[17] due to the poor leaving ability of the hydroxyl group, we sought to determine if electron-donor sensitizers would effect the rearrangement of *trans*-cinnamyl alcohol (3-*t*). Irradiation of a DMB–acetonitrile solution of 3-*t* for 2 h produced only trans–cis isomerization (87.4% and 12.6%, respectively). However, when this experiment was repeated with the protic solvent methanol in place of the aprotic media acetonitrile, photosolvolysis and rearrangement were observed (Scheme I). All experiments were performed on vigorously deaerated samples. There was little change in the product mixture when 0.054 g of potassium bicarbonate was added to the photolysis solution as an acid scavenger.[18] It thus appears that the use of protic media is beneficial for enhancing the hydroxyl leaving-group photolability to a point where solvolysis is possible. The energy of the excited state intermediate of 3-*t* and DMB is apparently not sufficient to effect the expulsion of the OH group in the highly polar but aprotic acetonitrile.

Finally, we have examined the DMB-photosensitized behavior of *trans*-cinnamyl methyl ether (Scheme II). As was observed with cinnamyl alcohol, irradiation of *trans*-cinnamyl methyl ether with DMB in acetonitrile produced only trans–cis isomerization (81.5% 4-*t*, 18.5% 4-*c*). Again, however, when methanol was used in lieu of acetonitrile, photorearrangement was observed. The possibility that adventitious amounts of photogenerated acidic species might give the observed rearrangements seems unlikely since a similar product mixture obtained when solid po-

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(17) For an exception to this, see ref 8. See also: Hixson, S. S.; Borovsky, J. *J. Chem. Soc., Chem. Commun.* 1975, 607.

(18) Cristol, S. J.; Lee, G. A.; Noreen, A. L. *Tetrahedron Lett.* 1971, 4175.

Table III. Effectiveness of Sensitizers at Effecting 1,3-Acetate Rearrangement of *trans*-Cinnamyl Acetate

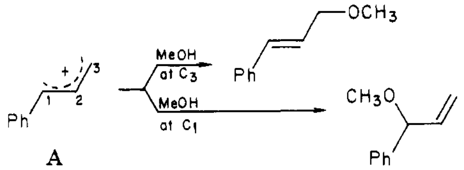
sensitizer	$E_{1/2}^{\text{oxidn}}$	E_S	E_T	calcd ΔG^a	observed 1,3-rearrangement
1,4-dimethoxybenzene	1.34^b	95.0		−8.99	+
toluene	1.98^c	105	82	−4.23	(+)
p-xylene	1.77^c	104	80.1	−8.07	+
N,*N*-dimethylaniline	0.78	94.5	76.6	−21.4	+
naphthalene	1.54^c	91	61	−0.37	(−)
2-methoxynaphthalene	1.52^d	86.8		+3.36	−
9,10-dimethoxyanthracene	0.98^d	74	42	+3.71	−
benzene	2.30^c	108	84	+0.15	−

[a] Calculated from Weller equation by using $E_{1/2}^{\text{redn}}$ for 1-*t* = −2.45 V.[22] [b] See ref 23. [c] See ref 24. [d] See ref 25.

tassium bicarbonate was present in the reaction medium.[18] It is interesting to note that for both **3**-*t* and **4**-*t* the amount of unrearranged starting material after 2-h irradiation is nearly the same in acetonitrile and in methanol.

Discussion

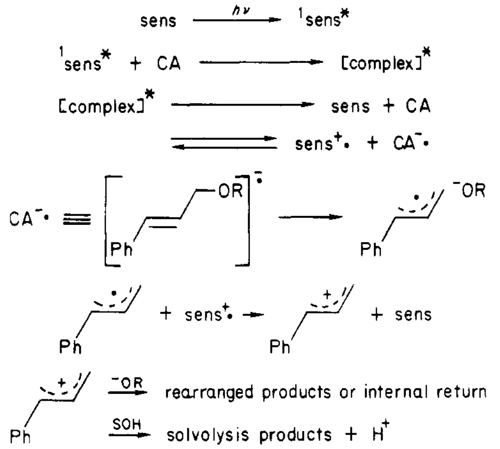
The data of our present work clearly seem to refute earlier published data[10,11] that indicated that triplet-sensitized irradiation of cinnamyl esters led to allylic rearrangement. Under these conditions we observed principally cis–trans isomerization about the C–C double bond, a process for which there is ample historical precedent.[19] Likewise, under direct irradiation conditions, where the excited-state singlet is produced, predominantly cis–trans isomerization was observed, accompanied by a very minor amount of allylic rearrangement. However, photosensitization of these cinnamyl alcohol derivatives with potential electron-donor compounds results in a fairly clean isomerization to allylic isomers and to solvolytic products. A priori, a number of reactive intermediates might be envisioned to account solely for the rearranged isomer. However, the formation of α-phenylallyl methyl ether (**6**) and of cinnamyl ether **4** during photolyses of **1** or **3** conducted in the presence of methanol, clearly seem to require the intermediacy of the cinnamyl cation.



A

The possible involvement of free-radical intermediates seems remote since addition of the free-radical scavenger, hydroquinone, had a negligible effect on the reaction rate or product yields. All of the irradiation product mixtures were relatively clean (in acetonitrile or in methanol), and products expected from free-radical intermediates (via decarboxylation of acetoxy or benzoyloxy radicals) were not detected. Our mass balances from these reactions were nearly quantitative within the limits of our analytical method (ca. ±5%). Furthermore, the major product in these photorearrangements is the contrathermodynamic isomer α-phenylallyl derivative.

Scheme III. Proposed Mechanism[a]



[a] sens = sensitizer. CA = cinnamyl alcohol derivative.

Another peculiar feature of these photoisomerizations was that classical excited-state energy transfer did not appear to apply.[19] The singlet and triplet excited-state energies of **1**-*t* have been estimated as 98.0[20] and 59.8 kcal/mol,[21] respectively. Since electronic energy transfer usually occurs when the energy of the sensitizer is ≥3 kcal/mol above that of the acceptor, it is clear with 1,4-DMB (E_s = 95 kcal/mol) that this condition cannot be met. Sensitization from the triplet state of donors does not appear to affect the 1,3-allylic isomerization either, as determined from our quenching studies with piperylene as well as lack of rearrangement with classical triplet sensitizers (such as acetone, E_T = 79 kcal/mol). Clearly, only certain sensitizers such as DMB, dimethylaniline, and *p*-xylene are capable of causing this rearrangement. We suggest that each of these sensitizers effects the 1,3-allylic isomerization via an electron-transfer process similar to that proposed by Ullman[8] for benzyl alcohol derivatives (Scheme III).

Using the free-enthalpy relationship developed by Weller[5] to account for electron-transfer fluorescence quenching

$$\Delta G\ (\text{kcal mol}^{-1}) = 23.06[E(D/D^+)_v - E(A/A^-)_v - 0.06] - \Delta E_{0,0}$$

where $E(D/D^+)$ and $E(A/A^-)$ are the one-electron oxidation and reduction potentials of respective donors and acceptors and $\Delta E_{0,0}$ is the excited-state energy of the sensitizer, we have found a remarkably accurate indication

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(19) Turro, N. J. "Modern Molecular Photochemistry"; Benjamin Cummings: Menlo Park, CA, 1978; Chapter 9.

(20) Estimated from the 0–0 absorption band of 1-*t* in CH_3CN (λ 292 nm).

(21) For values of β-methylstyrene, see: Cowan, D. O.; Baum, A. A. *J. Am. Chem. Soc.* **1971**, *93*, 1153. Also: Caldwell, R. A.; Sovocool, G. W.; Peresie, R. J. *Ibid.* **1973**, *95*, 1496. We thank a referee for pointing this reference out to us.

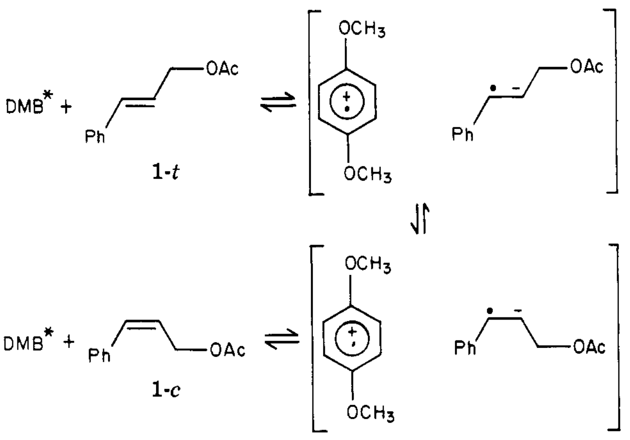
(22) Determined in acetonitrile with both a platinum wire and a dropping mercury electrode by using tetrabutylammonium perchlorate (0.1 M) as electrolyte vs. SCE reference electrode. We are indebted to Allan Fischer of MIT for determining this reduction potential.

(23) Zweig, A.; Hodgson, W. G.; Jura, W. H. *J. Am. Chem. Soc.* **1964**, *86*, 4124.

(24) Pysh, E. S.; Yang, N. C. *J. Am. Chem. Soc.* **1963**, *85*, 2124.

(25) Zweig, A.; Maurer, A. H.; Roberts, B. G. *J. Org. Chem.* **1967**, *32*, 1322.

Scheme IV



(and predictive capability) of whether or not a sensitizer can effect the 1,3-allylic rearrangement. These data are summarized in Table III.

Only in the case of toluene as photosensitizer was the predicted positive rearrangement found to be slow. We speculate that the weak absorption characteristics of this sensitizer relative to 1-*t* could account for the observed slow rate of rearrangement. In the case of naphthalene, which is predicted to be marginally exothermic in transferring an electron, we can detect the 1,3-allylic isomerization only after extended irradiation. This sluggish isomerization behavior probably reflects the inefficiency of the electron-transfer process. It was interesting to observe with naphthalene the very high cis/trans ratio of 1 that occurred via a presumed triplet energy pathway. Standard triplet-energy sensitizers gave a cis/trans ratio of 65:35, while naphthalene produced a corresponding ratio of 81:19. This behavior is analogous to previous measurements made on the cis–trans isomerization of stilbenes and α-methylstilbene[26] in which the triplet excited states for the cis isomers lay 9 and 6 kcal/mol, respectively, above those of the trans isomers. Hence, with sensitizers having triplet energies *just below* those of the cis isomer, only the trans isomer could be excited to its triplet state, and hence converted to more of the cis isomer. In our studies with cinnamyl acetate, where the triplet energy of the trans isomer is ca. 60 kcal/mol and the E_T of the cis isomer is ca. 70 kcal (by analogy with cis- and *trans*-β-methylstyrene[21]), naphthalene (E_T 61 kcal/mol) predominantly excites the trans isomer and the mixture becomes enriched in the cis isomer.

Another point of interest is the cis–trans isomerization of 1 with electron-donor sensitizers such as DMB. With all the sensitizers shown in Table III that can transfer an electron to 1, it is possible that a portion of the cis–trans isomerization can derive from classical triplet energy transfer ($E_{T(\text{sens})} > 3$ kcal + $E_{T(1\text{-}t \text{ or } 1\text{-}c)}$). Our quenching studies indicate that much of this trans–cis conversion derives from a quenchable triplet. However, above 0.1 M piperylene the quenching curve appears to change slope (from 11.1 to 7.8), indicating that above this concentration a certain amount of cis–trans isomerization may derive from a nonquenchable intermediate. One possibility for the alternative cis–trans isomerization pathway is that the radical anion of 1-*t* could undergo configurational isomerization to 1-*c* before decaying back to uncharged, ground-state intermediates (Scheme IV).

A similar explanation has been offered,[27,28] to explain configurational isomerization of alkenes induced by irradiation of charge-transfer complexes. As noted previously, radical anion intermediates of 1 also can dissociate to produce 1,3-isomerized products.

Further support for the involvement of electron-transfer photosensitization was provided by the observation that cinnamonitrile (CN) quenched the cis–trans as well as 1,3-allylic isomerization of 1 in a linear Stern–Volmer fashion. The reduction potential of CN ($E_{1/2}^{\text{redn.}} = -1.81$ V vs. SCE) indicates that both DMB* and $1^{-}\cdot$ should be quenched exothermically by CN.[29]

Irradiation of cinnamyl alcohol (**3**) or its methyl ether **4** in acetonitrile with DMB photosensitizer failed to yield any allylic isomerization. Only trans–cis isomerization was detected. However, when the protic solvent methanol was employed, both solvolysis and allylic rearrangement were observed. It is interesting to note also, that the previous, similar work of Ullman had been carried out in methanol.[8] We believe in all these cases that OH and OCH_3 groups by themselves are too difficult to remove in aprotic media. Protonation of these groups by solvent (MeOH), however, renders them sufficiently labile, so that they can undergo dissociation followed by the attendant trapping reactions. Similar observations have been reported by Cristol[9] for photosolvolyses of certain allylic substrates. The possibility that adventitious amounts of an acidic species were generated photochemically to effect these isomerizations seems remote since identical experiments run with excess, dry potassium bicarbonate gave essentially identical product mixtures. Also, identical reaction solutions kept in the dark did not produce any detectable rearrangements or solvolyses. The DMB-photosensitized reactions of **3** and **4** in methanol appear to involve photochemically induced expulsion of H-bonded OH and OCH_3 groups, followed by isomerization and by solvolyses. We have applied this observation to enhance the synthetic utility of these contrathermodynamic isomerizations. By irradiating DMB solutions of **1** or **3** in acetonitrile/acetic acid (9:1) for 48 h, we have obtained reaction mixtures containing 93% **5**, 4% 1-*c*, and 3% 1-*t*. Thus, synthetically useful quantities of α-phenylallyl products can be obtained when weakly acidic catalysts are employed in conjunction with suitable electron-donor sensitizers.

Conclusion

In all of the cinnamyl alcohol derivatives studied here (1–4), photosensitization with suitable electron-donor compounds appears capable of generating ionic intermediates. These intermediates have been observed to isomerize to thermodynamically less stable products and have been trapped by methanol as the methyl ether derivatives. The ability of the photosensitizers to effect these electron-transfer-initiated reactions correlates well with the enthalpy of reaction calculated by the Weller equation.

Experimental Section

Materials. *trans*-Cinnamyl acetate was obtained from K & K Chemicals (ICN Pharmaceuticals, Inc.) and purified by vacuum distillation, bp 114 °C (3.3 mm). The ^{1}H NMR IR, and mass spectra of this compound were identical with those for 1-*t* that were previously published.[14] *trans-cinnamyl* benzoate (2-*t*) was prepared from cinnamyl alcohol and benzoyl chloride by using

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[26] For a good review of this case, see: Lamola, A. A. "Energy Transfer and Organic Photochemistry"; Lamola, A. A., Turro, N. J., Eds.; Interscience: New York, 1969; Chapter 2.

[27] Arnold, D. R.; Wong, P. C. *J. Am. Chem. Soc.* **1979**, *101*, 1894.

[28] Roth, H. D.; Manion-Schilling, M. L. *J. Am. Chem. Soc.* **1979**, *101*, 1898.

[29] The possibility that CN could quench the electronic excited state of DMB also seems unlikely since E_s of is CN $\geq$ 95 kcal/mol, based on UV absorption measurements.

triethylamine as acid scavenger. The crude product was vacuum distilled (bp 156 °C (0.3 mm)) and gave ^{1}H NMR, IR, MS in agreement with authentic compound. *trans*-Cinnamyl methyl ether (**4**-*t*) was prepared via the PTC Williamson ether synthesis reported by Dubois and Freedman.[30] Reaction of cinnamyl alcohol (15 g, 0.112 mol) with methyl iodide (23.83 g, 0.168 mol) in 50 mL of dichloromethane and 50 mL of water containing sodium hydroxide (50 g, 1.25 mol) and tetrabutylammonium bisulfate (3.79 g, 0.011 mol) overnight at reflux gave a 91% yield of **4**-*t*, bp 55–56 °C (0.3 mm). The ^{1}H NMR, IR, and mass spectra were identical with that reported for pure **4**-*t*.[31] 1,4-Dimethoxybenzene was used as received from Aldrich (mp 56–57 °C). All reaction products were analyzed and characterized spectroscopically and found to be identical with previously reported compounds. Solvents were Burdick & Jackson, distilled-in-glass grade.

Equipment. Proton magnetic resonance spectra were obtained on a Varian EM-390 NMR spectrometer. Infrared spectra were run neat, between NaCl disks on a Beckman 4240 infrared spectrophotometer. Ultraviolet spectra were run in acetonitrile solvent in matching quartz cells on a Beckman Model DU-8 spectrophotometer. Analyses for most experiments were performed by gas chromatography using a Hewlett-Packard Model 5710 flame ionization gas chromatograph fitted with a 50-m glass capillary column (SP-2100 liquid phase). Peak areas were determined by electronic integration, and product yields were determined by comparing peak size relative to an added external standard (naphthalene). Product yields were corrected by individual product–standard response factors.

All reaction mixtures (except **2**) were analyzed by GC using the following conditions: 50-m SP-2100 capillary column, 1 mL/min He carrier flow, $T_{\text{det}} = T_{\text{inj}} = 250$ °C, $T_{\text{col}} = 120$ °C (2 min), program at 16°/min to 240 °C (2 min). The cinnamyl benzoate reaction mixtures were analyzed by using the following temperature program: $T_{\text{col}} = 120$ °C (0 min), programmed at 16°/min up to 240 °C (8 min).

Preparative separations were effected by high-pressure liquid chromatography using a Waters Prep LC/System 500 unit. GC/mass spectra determinations were obtained with a Hewlett-Packard Model 5985 GC/MS system, equipped with a 50-m glass capillary column (SP-2100 loading). Irradiations were performed with a Srinivasan-Griffin Rayonet Reactor (Southern N. E. Ultraviolet, Middletown, CT) equipped with eight 3100-Å low-pressure mercury lamps and a merry-go-round sample tube holder. Samples were placed in 18 × 150 mm Pyrex test tubes, deaerated by sparging with Ar for 10 min, and then sealed with rubber septum caps. Progress of the irradiation of these samples was monitored at frequent intervals by GC, and quantitative data were obtained before photoreaction had proceeded to 20% conversion of the starting material.

Reduction Potential Measurement on 1-*t*. Cyclic voltammetric data on **1**-*t* was obtained at MIT (courtesy of Prof. M. Wrighton) using a three-electrode cell with a Princeton Applied Research Model 170 electrochemistry system. A 10^{-3} M acetonitrile solution of **1**-*t* was evaluated both with a platinum disk and with a dropping mercury (0.5-s drop time) working electrode employing a platinum wire counterelectrode. A SCE electrode was used as a reference electrode and 0.1 M tetrabutylammonium perchlorate as supporting electrolyte. The agreement of $E_{1/2}^{\text{redn}}$ for both working electrodes was ±0.03 V.

Irradiation of *trans*-Cinnamyl Acetate (1-*t*) with 1,4-Dimethoxybenzene Sensitizer. Standard acetonitrile solutions were prepared from **1**-*t* (4.41 g, 2.50 × 10^{-2} mol) and from DMB (7.95 g, 5.76 × 10^{-2} mol) in 50-mL volumetric flasks. For DMB-sensitized irradiation of **1**-*t*, 1.0-mL aliquots of each of the above standard solutions were placed in 18 × 150 mm Pyrex test tubes and the contents diluted to 10.0 mL with additional solvent (CH_3CN, CH_3OH, C_6H_{12}). These solutions were deaerated by sparging with Ar gas for >10 min, capped, and irradiated for specified times. Reaction products were identified both by isolation from a preparative-scale photolysis experiment and by GC/MS. At the end of the irradiation period, 1.0 mL of a standard acetonitrile/naphthalene solution (4.37 g/50 mL) was added to the reaction mixture and the products analyzed by GC. Standard correction values for the detector response to both naphthalene and products were calculated to permit quantitative reaction yield determinations.

Table IV. Piperylene Quenching of 1,4-Dimethoxybenzene-Sensitized Irradiation of *trans*-Cinnamyl Acetate[a]

Q, mL	[piperylene], M	wt of **1**-*c* formed, mg	$(\Phi_0/\Phi_q)_{1\text{-}c}$	wt of **5** formed, mg	$(\Phi_0/\Phi_q)_5$
0	0	9.07	1.00	6.02	1.00
0.5	0.033	6.22	1.46	6.05	0.995
1.0	0.066	4.98	1.82	6.25	0.963
3.0	0.198	2.87	3.16	5.14	1.17
5.0	0.330	2.20	4.12	4.98	1.21
8.0	0.529	1.57	5.78	4.07	1.48

[a] [**1**-*t*] = 5.01 × 10^{-2} M; [DMB] = 0.115 M; all samples irradiated for 80.0 min with eight 3100-Å Rayonet lamps.

Piperylene Quenching of 1,4-Dimethoxybenzene-Sensitized Irradiation of *trans*-Cinnamyl Acetate (1-*t*). Freshly distilled piperylene (1.12 g, 1.65 × 10^{-2} mol) was diluted to 25 mL with acetonitrile to make a standard quencher solution (Q). To 18 × 150 mm Pyrex test tubes containing 1.0 mL each of the standard **1**-*t* and DMB solutions was then added varying amounts of solution Q and sufficient acetonitrile to make the total solution volume in each tube equal 10.0 mL ([**1**-*t*] = 5.01 × 10^{-2} M, [DMB] = 0.115 M). The samples were run in duplicate for each piperylene concentration and data obtained from the average of at least three GC analyses. Table IV summarizes the data from these experiments.

Preparative-Scale Irradiation of *trans*-Cinnamyl Acetate Sensitized by 1,4-Dimethoxybenzene. *trans*-Cinnamyl acetate (3.01 g, 0.0171 mol) and 1,4-dimethoxybenzene (2.07 g, 0.015 mol) dissolved in acetonitrile (225 mL) were placed in a Pyrex glass reactor, which was fitted with a 450-W Hanovia mercury arc UV lamp, encased in a Pyrex immersion well (UV cutoff at 300 nm). The solution was stirred magnetically and sparged continuously with a stream of argon. After irradiation for 220 min, the reaction was worked up by solvent removal and by HPLC (solvent system 90:10 hexane/diethyl ether) separation of the reaction components. Spectra of the isolated pure components were identical with those previously reported.[14]

Irradiation of *trans*-Cinnamyl Acetate in Acetonitrile/Acetic Acid. *trans*-Cinnamyl acetate (0.94 g, 5.34 × 10^{-4} mol) and 1,4-dimethoxybenzene (0.157 g, 1.14 × 10^{-3} mol) dissolved in acetonitrile (9.0 mL) and acetic acid (1.0 mL) were placed in a Pyrex tube, deaerated with argon for 15 min, capped with a rubber septum, and irradiated with eight 3100-Å Rayonet lamps for 48 h. The reaction mixture was analyzed by GC to contain 93.3% **5**, 3.6% **1**-*c*, and 3.1% **1**-*t*.

Irradiation of *trans*-Cinnamyl Benzoate (2-*t*) with 1,4-Dimethoxybenzene Sensitizer. A solution of **2**-*t* [0.103 g, 4.32 × 10^{-4} mol), purified by preparative HPLC] and DMB (0.152 g, 1.10 × 10^{-3} mol) in acetonitrile was placed in an 18 × 150 mm Pyrex test tube, purged with Ar for 10 min, capped with a rubber septum cap, and irradiated with eight 3100-Å Rayonet lamps for 120 min. At the end of the irradiation, 1.0 mL of a standard naphthalene solution was added and the solution quantitatively analyzed by gas chromatography to contain 4.2% **7**, 18.3% **2**-*c*, and 77.4% **2**-*t*.

Irradiation of *trans*-Cinnamyl Alcohol (3-*t*) Sensitized by 1,4-Dimethoxybenzene in Acetonitrile. A 10.0-mL acetonitrile solution of **3**-*t* (Aldrich, 0.103 g, 9.40 × 10^{-4} mol) and DMB (0.160 g, 1.16 × 10^{-4} mol) was deaerated with Ar for 10 min, capped, and irradiated for 120 min with eight 3100-Å Rayonet lamps. At the end of this time, 1.0 mL of a standard naphthalene solution was added and the reaction mixture quantitatively analyzed by gas chromatography to contain only 12.6% **3**-*c* and 87.4% **3**-*t*.

Irradiation of *trans*-Cinnamyl Alcohol (3-*t*) Sensitized by 1,4-Dimethoxybenzene in Methanol. A 10.0-mL methanol solution of **3**-*t* (0.0912 g, 6.81 × 10^{-4} mol) and DMB (0.151 g, 1.09 × 10^{-3} mol) was deaerated with Ar for 10 min, capped, and ir-

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(30) Freedman, H. H.; Dubois, R. A. *Tetrahedron Lett.* **1975**, 3251.

(31) Hart, H.; Brewbaker, J. L. *J. Am. Chem. Soc.* **1969**, *91*, 716.

radiated for 120 min with eight 3100-Å Rayonet lamps. Addition of 1.0 mL of standard naphthalene solution to the reaction mixture permitted quantitative GC analysis, which indicated the following composition: 7.9% **3**-*c*, 85% **3**-*t*, 3.6% **4**-*t*, and 3.4% **6**.

Irradiation of *trans*-Cinnamyl Methyl Ether (4-*t*) Sensitized by 1,4-Dimethoxybenzene in Acetonitrile. A 10.0-mL acetonitrile solution of **4**-*t* (0.0837 g, 5.66×10^{-4} mol) and DMB (0.171 g, 1.24×10^{-3} mol) was deaerated with Ar for 10 min, capped, and irradiated for 120 min with eight 3100-Å Rayonet lamps. After addition of 1.0 mL of a standard naphthalene solution, the reaction mixture was quantitatively analyzed by GC to contain 81.5% **4**-*t* and 18.5% **4**-*c* only.

Irradiation of *trans*-Cinnamyl Methyl Ether (4-*t*) Sensitized by 1,4-Dimethoxybenzene in Methanol. A 10.0-mL methanol solution of **4**-*t* (0.0910 g, 6.15×10^{-4} mol) and DMB (0.167 g, 1.21×10^{-3} mol) was deaerated with Ar for 10 min, capped, and irradiated for 120 min with eight 3100-Å Rayonet lamps. At the end of this time, 1.0 mL of a standard naphthalene solution was added and the reaction mixture was quantitatively analyzed by GC to contain 5.8% **6**, 13.6% **4**-*c*, and 80.6% **4**-*t*.

Registry No. **1**-*c*, 77134-01-1; **1**-*t*, 21040-45-9; **2**-*t*, 50555-04-9; **3**-*t*, 4407-36-7; **4**-*t*, 22688-03-5; **5**, 7217-71-2; acetone, 67-64-1; 1,4-dimethoxybenzene, 150-78-7; 9,10-dimethoxy-2-ethylanthracene, 26708-04-3; 2-methoxynaphthalene, 93-04-9; *N*,*N*-dimethylaniline, 121-69-7; naphthalene, 91-20-3; *p*-xylene, 106-42-3; toluene, 108-88-3; 9,10-dimethoxyanthracene, 2395-97-3; benzene, 71-43-2; piperylene, 504-60-9.

2-Methyl Substituent Effects in the Antihomoaromatic Cycloprop[2,3]inden-1-yl Cation

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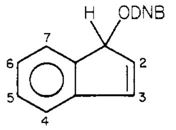
The rates and products of hydrolysis of the *endo*- and *exo*-2-methylcycloprop[2,3]inden-1-yl 3,5-dinitrobenzoates in 80% aqueous acetone have been determined. These are compared with similar data for the corresponding unsubstituted esters and for the 1-methyl-substituted and unsubstituted *endo*- and *exo*-2-bicyclo[3.1.0]hexyl 3,5-dinitrobenzoate model systems. This was done in connection with reports that toward acid-catalyzed epimerization in 50% aqueous dioxane at 80 °C 2-methyl substitution caused a 250-fold rate deceleration in the *endo*-cycloprop[2,3]inden-1-ol system. For the endo 3,5-dinitrobenzoates the 2-methyl substituent did produce a rate decrease; however, this was only by a factor of about 1.2 at 80 °C. In the 2-bicyclo[3.1.0]hexyl model system, the corresponding 1-methyl substitution caused approximately a 2-fold rate increase.

Introduction

Several papers have appeared from our laboratory during the past 5 years concerning the effects of methyl substitution on the rates of formation and products of reaction of the antiaromatic inden-1-yl and antihomoaromatic cycloprop[2,3]inden-1-yl cations. For example, Friedrich and Tam[1] found that methyl substitution at the 5- and 3-positions of inden-1-yl 3,5-dinitrobenzoate (**1**) resulted in rate accelerations at 21 °C of about 70 and 1100, respectively, for solvolyses in trifluoroethanol. These were similar in magnitude to those found for methyl substitution in the corresponding nonantiaromatic model systems **2** and **3**. Thus, it was concluded that the nature and magnitude of charge delocalization into the benzene-ring and double-bond carbons of the inden-1-yl cation are virtually unaffected by antiaromatic effects.



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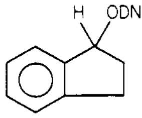

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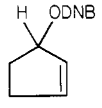

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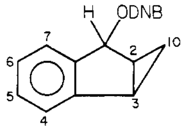
In contrast to the results obtained with the inden-1-yl system, Friedrich et al.[2] found with cycloprop[2,3]inden-1-yl 3,5-dinitrobenzoate (**4**) that methyl substituent effects do not parallel those seen with the model system **5**. For example, in 80% aqueous acetone at 80 °C, 3- and *anti*-10-methyl substitution caused rate accelerations of about 1.2 and 17, respectively, in the cycloprop[2,3]inden-]-yl system. On the other hand, for the corresponding 5- and *anti*-6-methyl-substituted 2-bicyclo[3.1.0]hexyl 3,5-dinitrobenzoate model systems, rate accelerations of 22[3] and 8.3,[4] respectively, were observed under the same reaction conditions.



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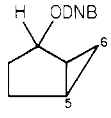

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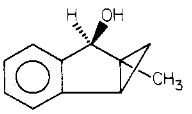
In connection with the latter results, it was of considerable interest to note a report in 1981 by Răzuş and coworkers[5] of their investigations of the magnitudes of methyl substituent effects in perchloric acid catalyzed isomerizations of the 2- or 3-methyl-substituted *endo*-cycloprop[2,3]inden-1-ols (**6** and **7**) in 50% aqueous diox-



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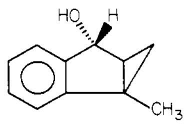

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(1) Friedrich, E. C.; Tam, T. M. *J. Org. Chem.* **1982**, *47*, 315.

(2) Friedrich, E. C.; Taggart, D. B.; Saleh, M. A. *J. Org. Chem.* **1977**, *42*, 1437.

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